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METHOD FOR PRODUCING SPHERICAL OXIDE GELS

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This invention concerns a method for producing spherical hydrogels.

Up to now it has been conventional to make spherical silica gels by dripping a silicic acid hydrosol into a liquid, for example into an organic solution, where the resulting spherical hydrosols are suspended in this liquid and, because of the effect of the pH of the hydrosol, the temperature of the liquid, the substance dissolved in this liquid and the dissolved material itself, such as an aluminum salt, in these hydrosols, are converted, whereupon the spherical hydrogels obtained in this way are then washed and dried, so that one obtains spherical gels.

However, it is practically impossible to separate the organic liquid or the organic solvent from the spherical gels through this method, so that the gels are contaminated and discolored or blackened. The use of these spherical gels also results in substances dried with these gels being contaminated, and metal ions such as aluminum ions that may be present in the solution cause increased acidity on the surface of the gels. Moreover, the value of the specific density of the hydrosol and the oily liquid medium are pretty much the same, so that the hydrosols and hydrogels and the oil and the hydrogels are in contact with each other and mix with each other, so that uniform compositions can be obtained only with great difficulty. Moreover, in the production of spherical gels that have to be gelated in an oily medium, considerable restrictions have to be made as a result of the physical conditions of the raw material that is used, namely with regard to concentration and temperature, and with respect to the mixture ratio of raw materials of this kind, so that the manufacture of high grade gels is not possible.

In addition to these many undesirable disadvantages of the known methods is the use of an oily solution, which considerably complicates the method and necessitates a great deal of care, since substances that are combustible or hazardous to health are used.

This invention now has the task of proposing a method with which no organic solution has to be used, so that the above disadvantages of the known methods are overcome.

In carrying out the invention, an acid with a given concentration of, for example, a normality from 2 to 20 or a mixture of this acid with a metal salt, and a solution of a nonmetallic weakly acid alkali salt are brought together in any concentration under high pressure in a mixing device (for example a two-cylinder nozzle made of an acid- and alkali-resistant material) and immediately mixed with each other, whereupon the mixture is sprayed from the nozzle into air (or into another gas atmosphere), where it forms spherical particles of a hydrogel. The particles fall into a vessel containing acidified water with an appropriate pH value, where the particles are collected.

The pH value of the ejected or sprayed mixture can be adjusted by the appropriate change of the ratio of the amounts of these two solutions. Moreover, the temperature of the hydrosol can be raised somewhat over that of the two solutions before mixing, specifically to an appropriate temperature through which the temperature of these two solutions can be controlled.

Accordingly, a hydrosol with uniform composition is obtained, and the time necessary for the gelation of the hydrosol can be maintained in a range between immediate and 10 seconds, by regulating the temperatures of the two solutions and their relationship. The actual flight path (or spray path) from 5-30 m and the time necessary for the downward fall of the gels (from about 2-10 sec) and the size of the area where the gel falls, as well as the diameter of the spherical hydrogel and its distribution can be regulated by the appropriate choice of the shape of the nozzle, by the projection or jutting of the nozzle orifice and the pressure with which the solutions are fed to the device. Disadvantageous effects like drying out of the surface on these spherical hydrogels because of the motion in air or gas are not observed, since these hydrogels immediately sink in water. The possibility of any kind of disadvantage disturbances can be affected even more effectively through a precise choice of the type and temperature of the gaseous atmosphere.

The hydrogels obtained in this way are then aged, washed, dried and converted to spherical gels. The resulting spherical gels are equal to or better than Gel Type A or Gel Type B according to the Japanese Industrial Standard, and do not contain any organic or inorganic contaminants. These spherical gels have a diameter of about less than 0.1 up to 5 mm and have an adsorption capacity of 100%.

Example 1

A 3-N dilute sulfuric acid was fed at pressure of 1 kg/cm^2 at 20°C and a 2-N sodium silicate solution was fed at a constant pressure of 5 kg/cm^2 at 20°C to a concentric twin cylinder nozzle with a nozzle diameter of 4 mm. The temperature of the mixture is 42°C and the throughput rate was set to 3 Σ/min. The pH was 8 or 9; about 1 sec was needed for the solution to gel. This meant that the flight path had to be 7 m. A container with a diameter of 1.5 m containing acidified water with a pH of 2 was set at the site where the gels fell in order to collect the gels.

The hydrogels produced in this way had a uniform composition, were transparent and had a diameter of 6-1 mm. Outstanding spherical gels that were colorless and transparent and had a diameter of 0.5-3 mm were obtained by washing and drying the aged hydrogels. The adsorption capacity of the gels is 110 mg H_2O/g SiO_2 at 20% relative air humidity or 330 mg H_2O/g SiO_2 at 90% relative air humidity. This meets the specifications of the Japanese Industrial Standard. After activation, the chemical composition of these spherical gels corresponded to nearly pure silicic acid consisting of more than 99.8% SiO_2. The volume reduction during activation was about 7%, which was essentially due to loss of water. When these gels are heated in air to 100-400°C, they do not discolor like the spherical gels made by the known methods.

Example 2

The procedure in accordance with Example 1 was followed; the water container for collection of the gels contained water with a pH of 7. The spherical gels had properties that corresponded to silica gel Type B that is suitable as an adsorption agent in accordance with the Japanese Industrial Standard; the adsorption properties were 50 mg H_2O/g SiO_2 at 20% relative air humidity and 600 mg H_2O/g SiO_2 at 90% relative air humidity.

Example 3

A 2-4-N sulfuric acid was fed under constant pressure between 2 and 5 kg/cm^2, to a concentric double cylinder nozzle together with a 3- to 5-normal sodium silicate solution likewise under a pressure of 2 to 5 kg/cm^2. The temperature of the mixture was about 40°C, while the throughput rate of the mixture was set to 2-4 Σ/min.

The pH was between 4 and 6; 0.5-1 sec was required for gelation of the solution, which corresponded to a flight path of 2-5 m. The pH of the water used to collect the falling spherical silicic acid hydrogel particles in the container corresponded approximately to that of the hydrogels.

The fallen hydrogels were kept for 1-10 h at the appropriate temperature, in water that had approximately the same pH value as the water in the container; then they were washed with water. The pH of the wash water corresponded initially to that of the water in the container and was then adjusted to a desired value between 2 and 11. After washing, the hydrogels were dried and spherical gels were obtained. If the pH of the wash water at the end of the washing operation had an approximate pH value of 3, the adsorption property of the resulting silica gel corresponded to the properties of a silica gel of Type A in accordance with the Japanese Industrial Standard. At a pH of 10, the adsorption properties corresponded to those of silica gel Type B according to the Japanese Industrial Standard.

Claims

1. A method for producing spherical hydrogels, which is characterized by the fact that an acid or a mixture of an acid and a metal salt and an aqueous solution of an alkali salt of a nonmetallic weak acid are fed together under pressure into a mixing device, immediately mixed in this mixing device and the resulting mixture is sprayed into a gas atmosphere, so that the sprayed mixture of the hydrosol is gelatinized during the flight through the gas atmosphere, whereupon the resulting spherical hydrogel particles are collected in a vessel containing acidified water.

2. A method as in Claim 1, which is characterized by the fact that the mixture is sprayed through the atmosphere for 2 to 10 seconds.